Insitu/Operando Methods at the NSLSII ISS Beamline: Reactors, Detectors, and Applications

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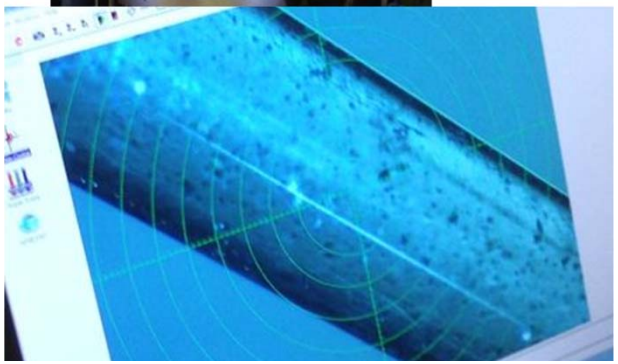
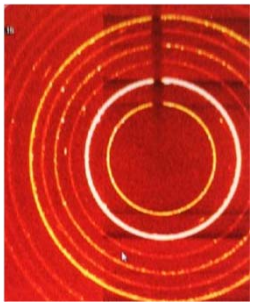
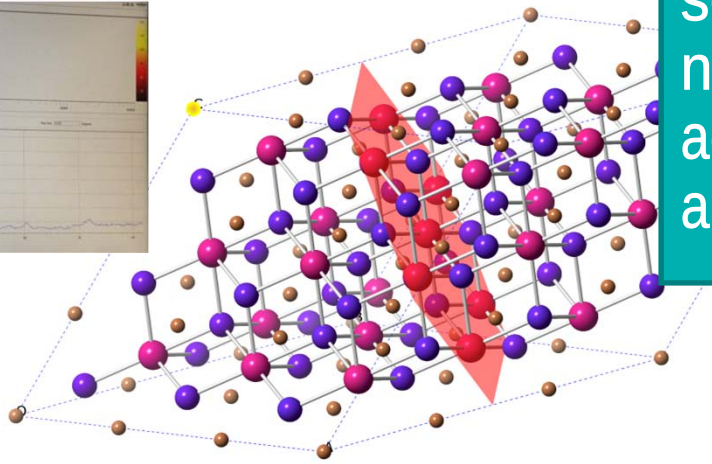
What makes the success of a commercial instrument?



The Approach:

1. Fully integrated system: source, optics, detector sample handling
2. Easy handling: semi automatic sample alignment, easy setup of scans, calibrated instrument, easy to display "data-content"
3. Providing "wanted information" not raw data: providing interface to simulation tools, providing quantitative numbers (like compound analysis), visualizing the results.
4. Availability





Key is to focus on the scientific problem and not on the data acquisition and data analysis.

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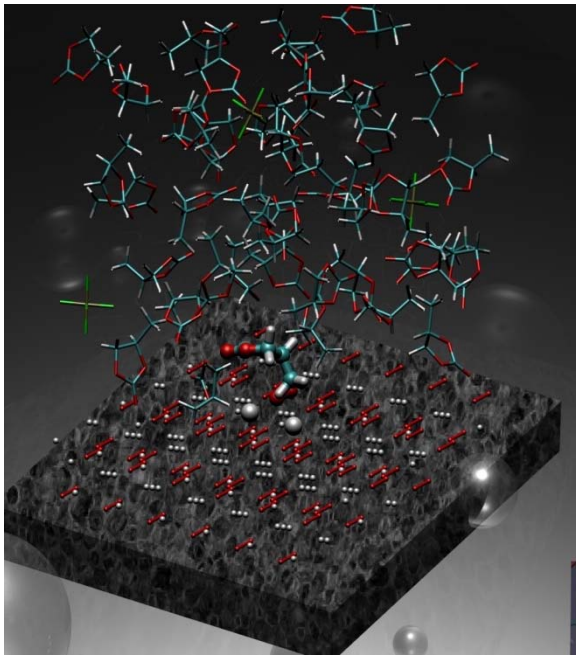
In-situ, In-operando, In-vitro & Co

Scientific Goal of many synchrotron experiments:

Investigating correlations between structure, chemical composition and functionality in

"Real Worlds Materials and Under Realistic Environment"



DOI: 10.1002/chem.201103057

Why can we approach these difficult problems at the X-ray facilities:

- Significant increase of photon flux (6-8 orders of magnitude)
- Better defined beam properties (polarization, energy resolution, coherence, beam size, energy range)
- Well trained service team

What can we learn from lab-instrumentation:

- High availability with fast turn-over (especially with short funding cycles and industrial research)
- Optimized detection, focusing and sample handling system
- Dedicated instrumentation, fully integrated in the data acquisition system and fully calibrated
- Don't focus on raw data but provide the information which is needed (for example bonding distances instead of EXAFS spectra)

What do we need to provide

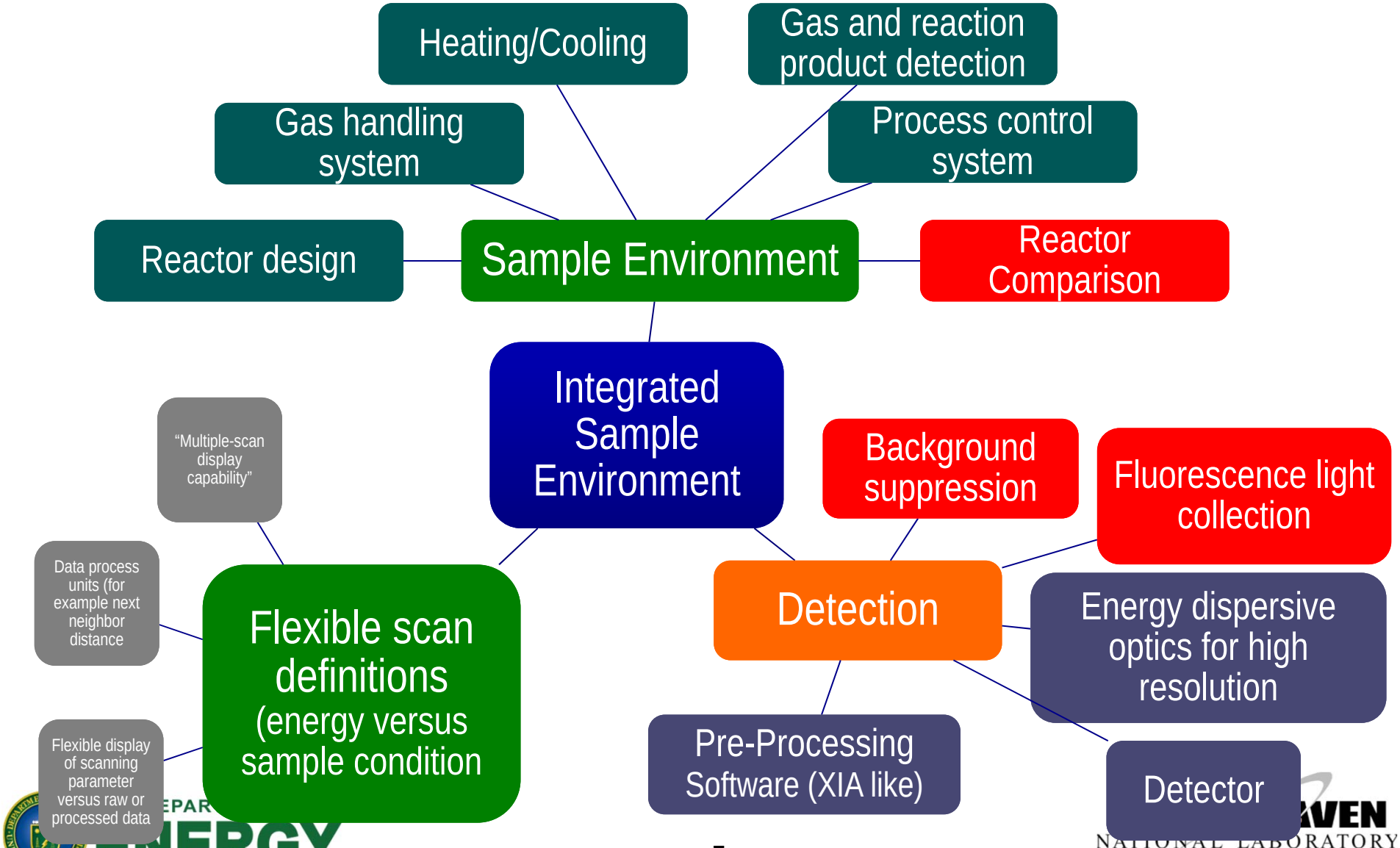
So far we delivered to users:

- Excellent sources
- Increasingly stable and sophisticated photon delivery systems
- Some in-situ sample environments
  - early examples are the Lydle detector with in situ catalysis reactor
  - Increasingly sophisticated in-operando setups
  - Some additional sample preparation tools

What is missing?

- Optimized detection/sample environment/ focusing
- Sample environment which is integrated into data acquisition system
  - Appropriate atmosphere, temperature and pressure
  - Optimized sample preparation, aging, conditioning facilities (off line from beamline)
  - Recording and controlling of all processing by the data acquisition system
- Software which allows
  - To display important properties like next neighbor distances, composition of compounds, …….
  - To correlate the incoming data online with databases and simulation packages

What has "Priority": Detection, Sample environment, or Focusing



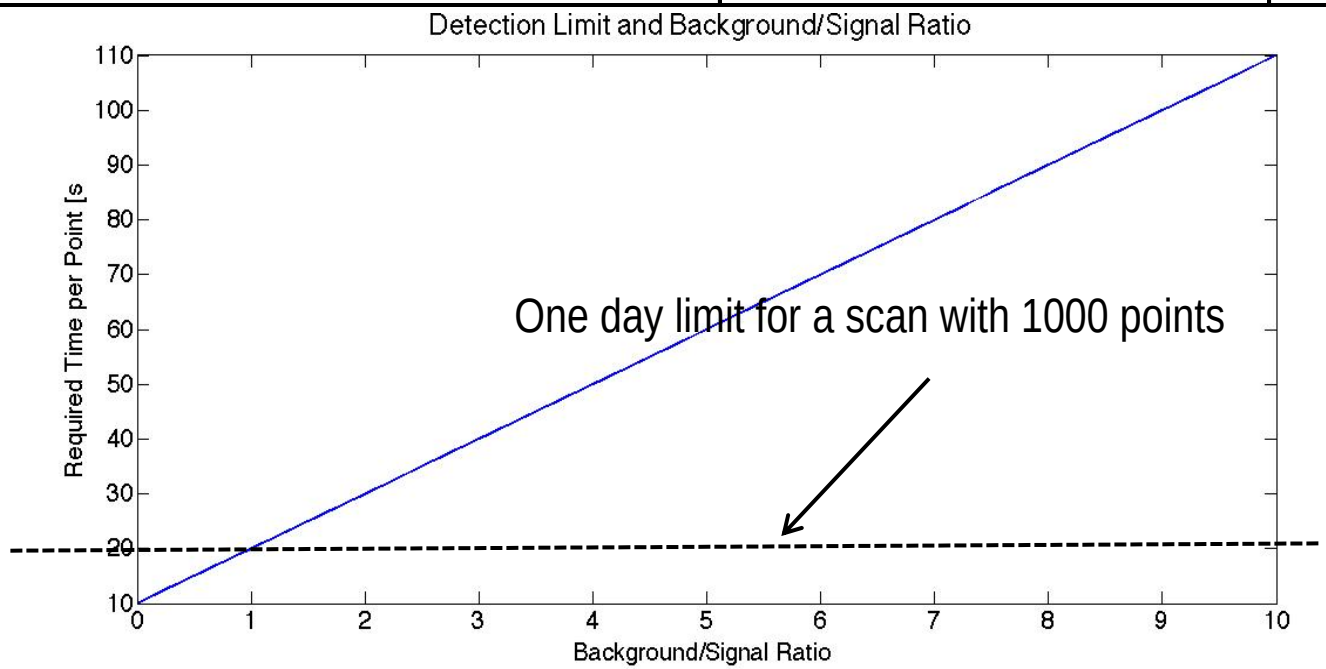
The Detection Problem in Spectroscopy

Sample damage is not dependent on beam intensity but on dose:

- Valid as long “multi-photon” absorption is negligible (valid for most synchrotron experiments)
- Sample exposure should be allowed only during data acquisition (alignment with optimized (reduced dose)
- Optimized detector needs
  - Excellent detection efficiency: large solid angle, high photon detection probability
  - High background suppression

SIGNAL TO BACKGROUND RATIO AND REQUIRED TIME (DOSE)

Property	Ultra dilute	Standard sample
Incoming intensity	10^{14} Photon/s	
Signal (Fe K_α)	10^{7} Photons/s	10^{10} Photons/s
Background (Thomson & Compton)	$2x10^{11}$ Photons/s	~ 10^{11} Photons/s



Model assumptions:

- a 1μmol/L solution of Fe in H_2O (Ultra dilute case)
- 10^{14} Photons/s on the sample
- 1% detection efficiency
- 0.1% statistical noise per point

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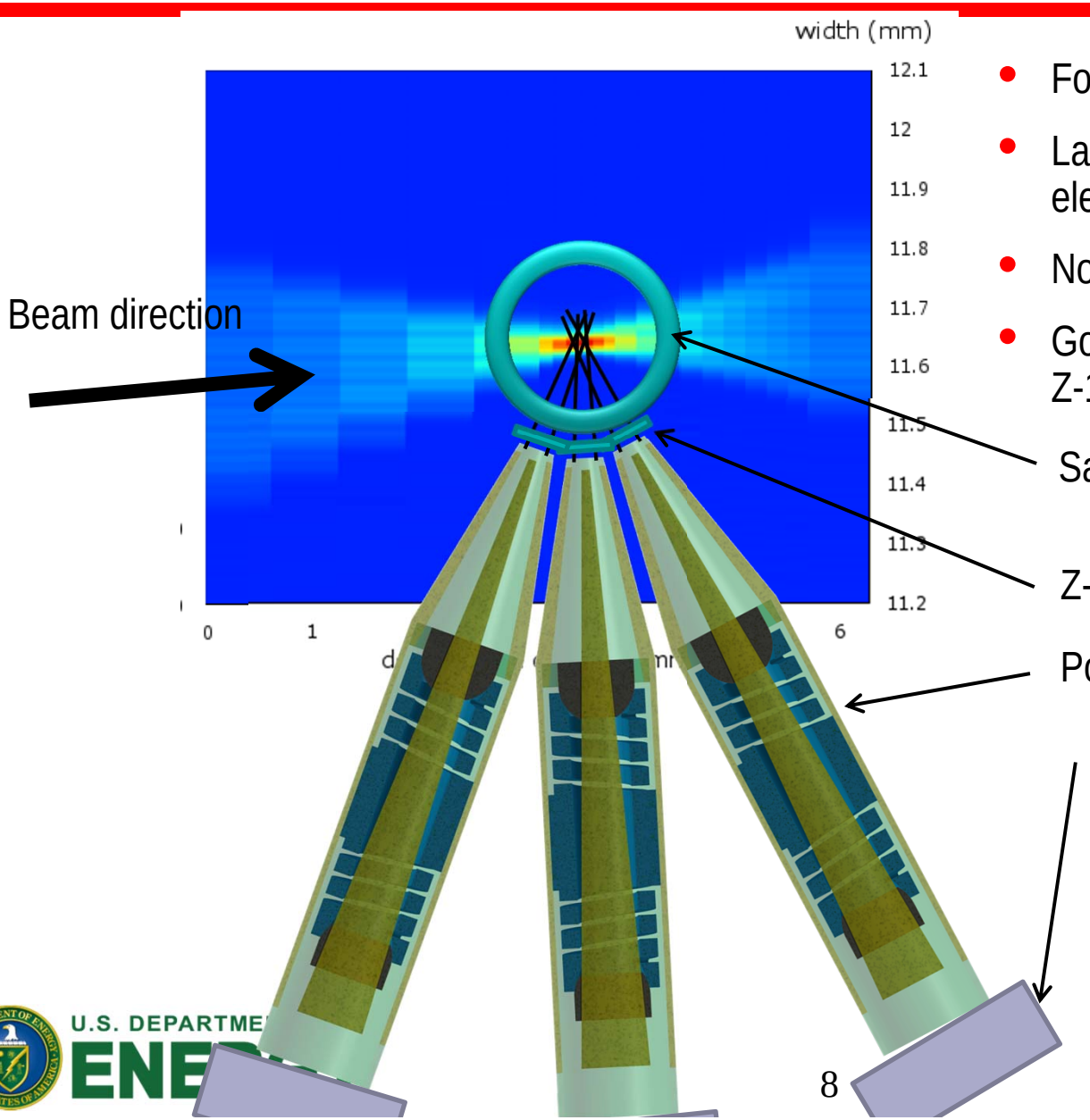
CONFOCAL DETECTION TO SUPPRESS BACKGROUND AND SIMPLIFY OPERATIONS



- Focus size: 25μm
- Large angle coverage by multi element system
- No background from reactor wall
- Good elastic line suppression with Z-1 filter

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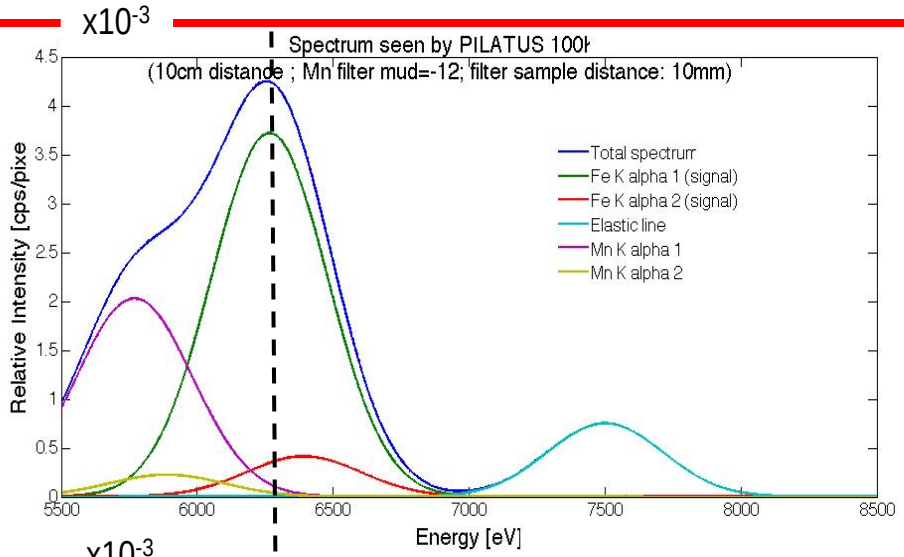
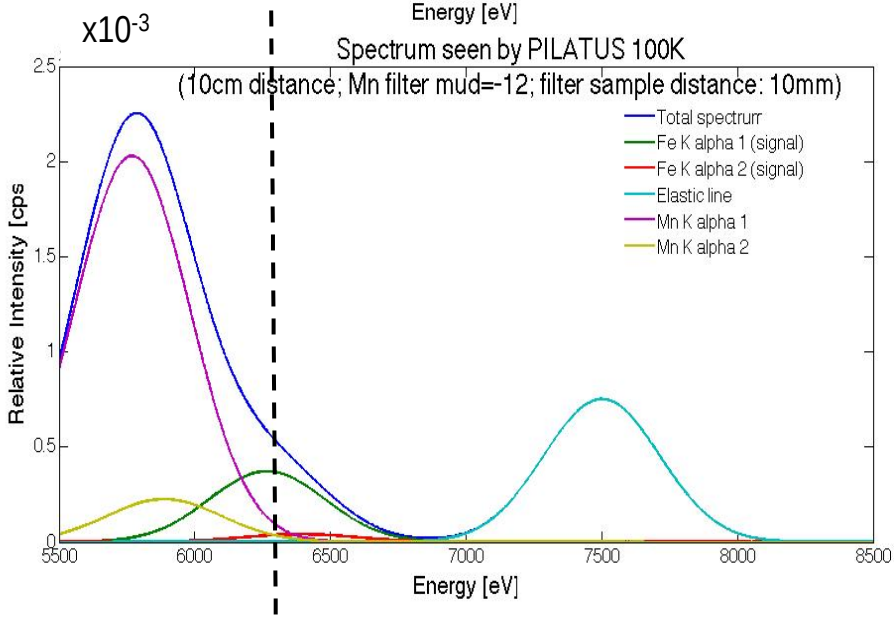
SPECTRUM AT THE DETECTOR SIDE

10μmol/L



1μmol/L



"good photons"

Models assumes ultra dilute sample (Fe in HO2) from slide 6

- Count rate normalized to single capillary
- Spectrum is assuming 500eV energy resolution of detector
- 10μmol/L can be easily detected; 1μmol/L is difficult but possible
- Background suppression of elastic is about 10^3!

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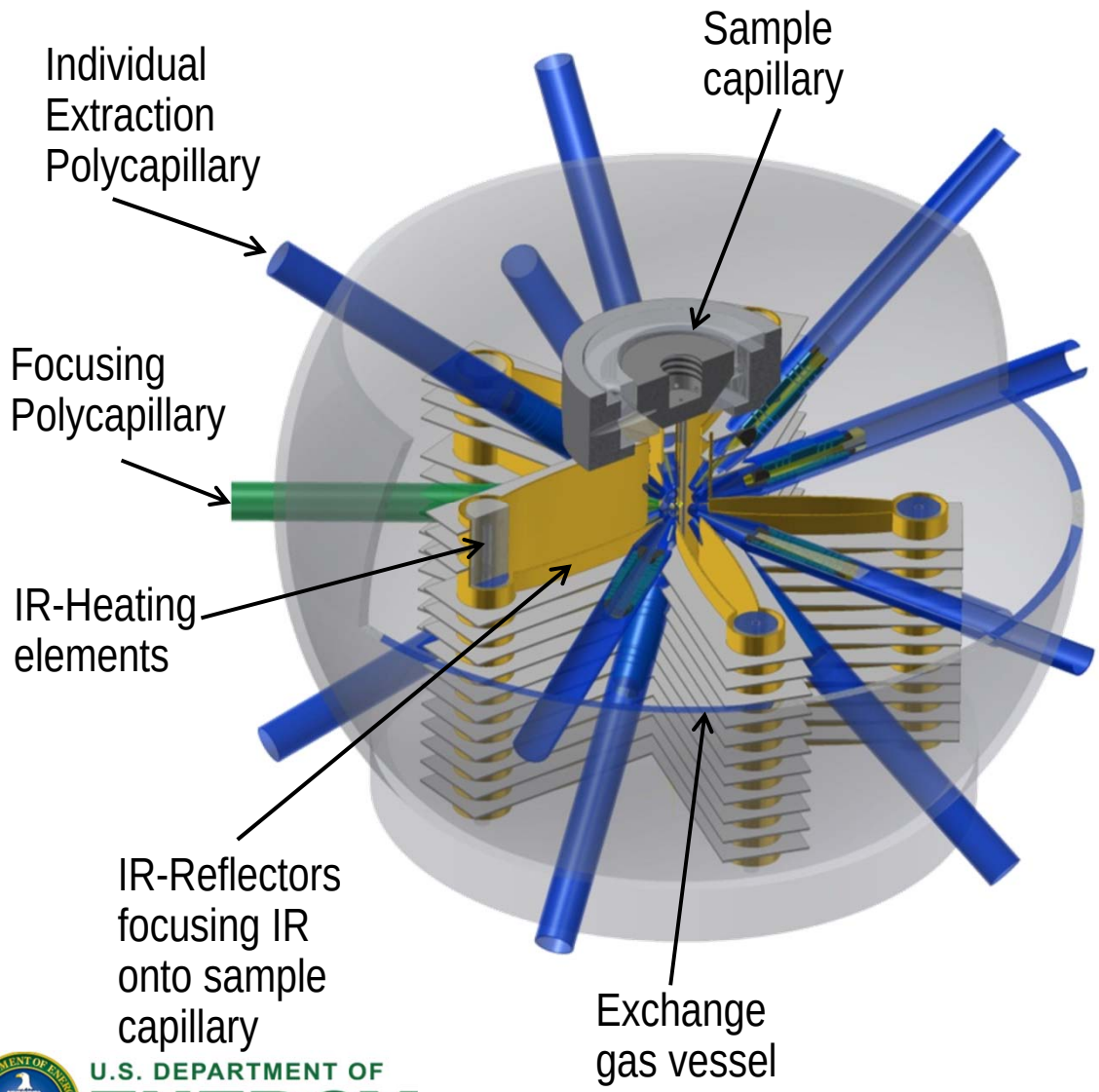
HOW TO COMBINE SAMPLE ENVIRONMENT AND LARGE SOLID ANGLE ACCEPTANCE



Integrated detection system

- Confocal detection system
  - "self aligned" optics "independent" from source movements (perfect for high heat load optics)
  - Reduction of background from complex sample environments
- 14 extraction systems allow a solid angle acceptance of 25%
  - Efficiency corrected ~10%-5%
  - Active volume ~ 50x50x50μm^3

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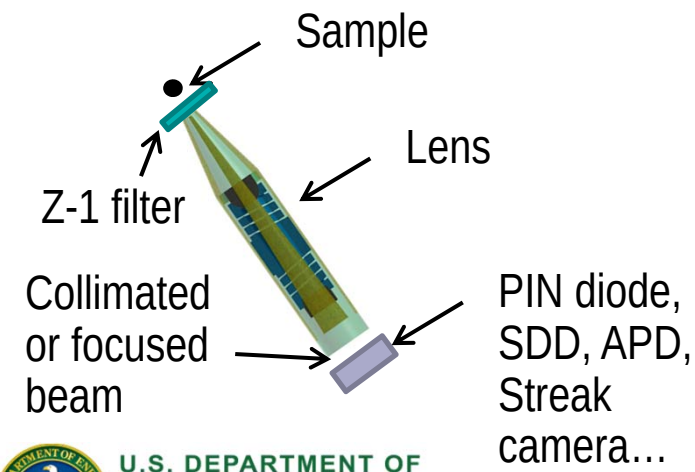
WHAT TO DO WITH THE EXTRACTED FLUORESCENCE PHOTONS:

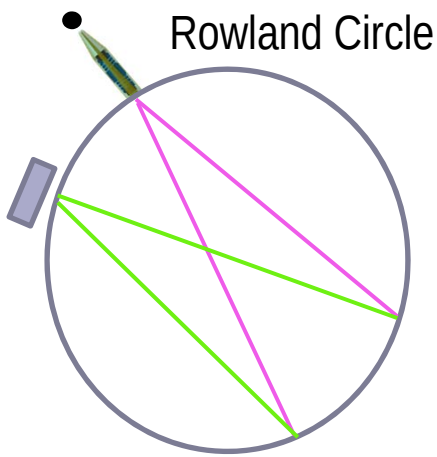
Modified Stern-Heald detector

- Polycapillary acts as soller slit
- Perfect for diluted systems with eladtic and compton backkground
- Using full lenses will allow small detectors and “extreme” detectors like steak cameras



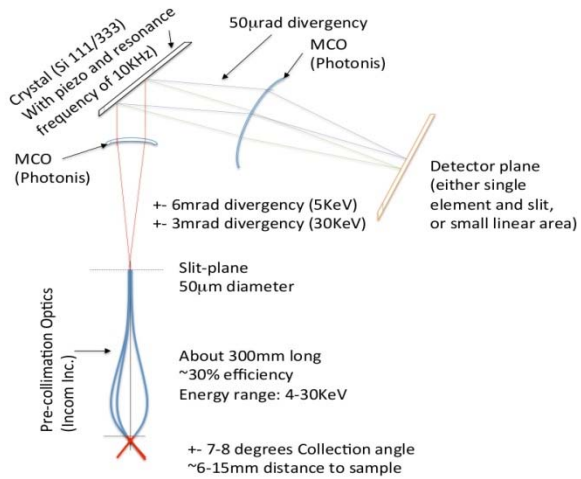
Conventional Spherical Back Scattering Analyzer

- Using full lens results with virtual source size and divergence optimal for 1m SBA
- Gain of about 5 (reference G. Seidler)
- Larger distance between detector and sample environment



A new spectrometer idea: Czerny-Turner Spectrometer

- Optical collimation
  - Using state of the art poly capillary optics and Multi-channel plate optics
  - Allows flat crystals and very easy energy range



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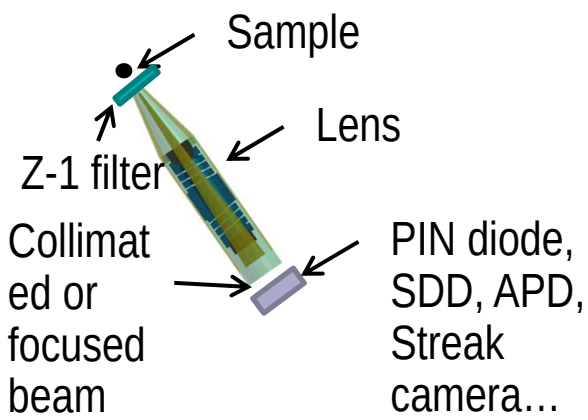
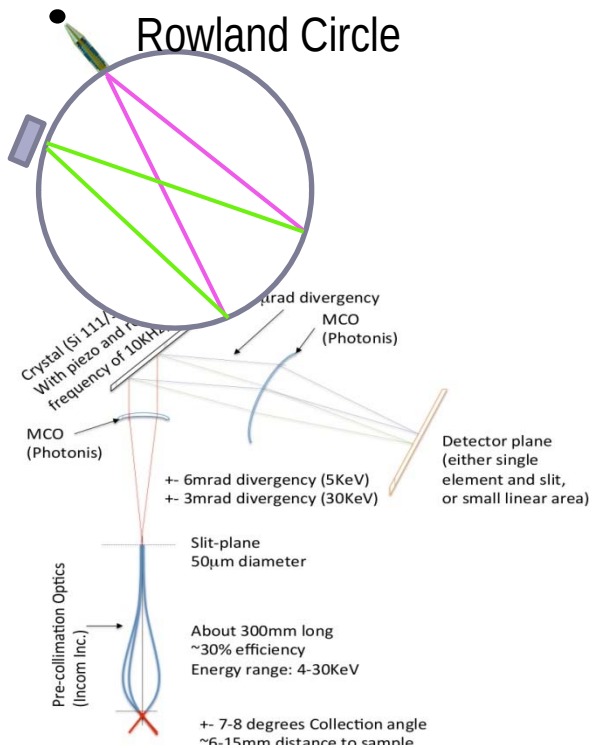
DIGITAL PROCESSING: THE RAW DATA

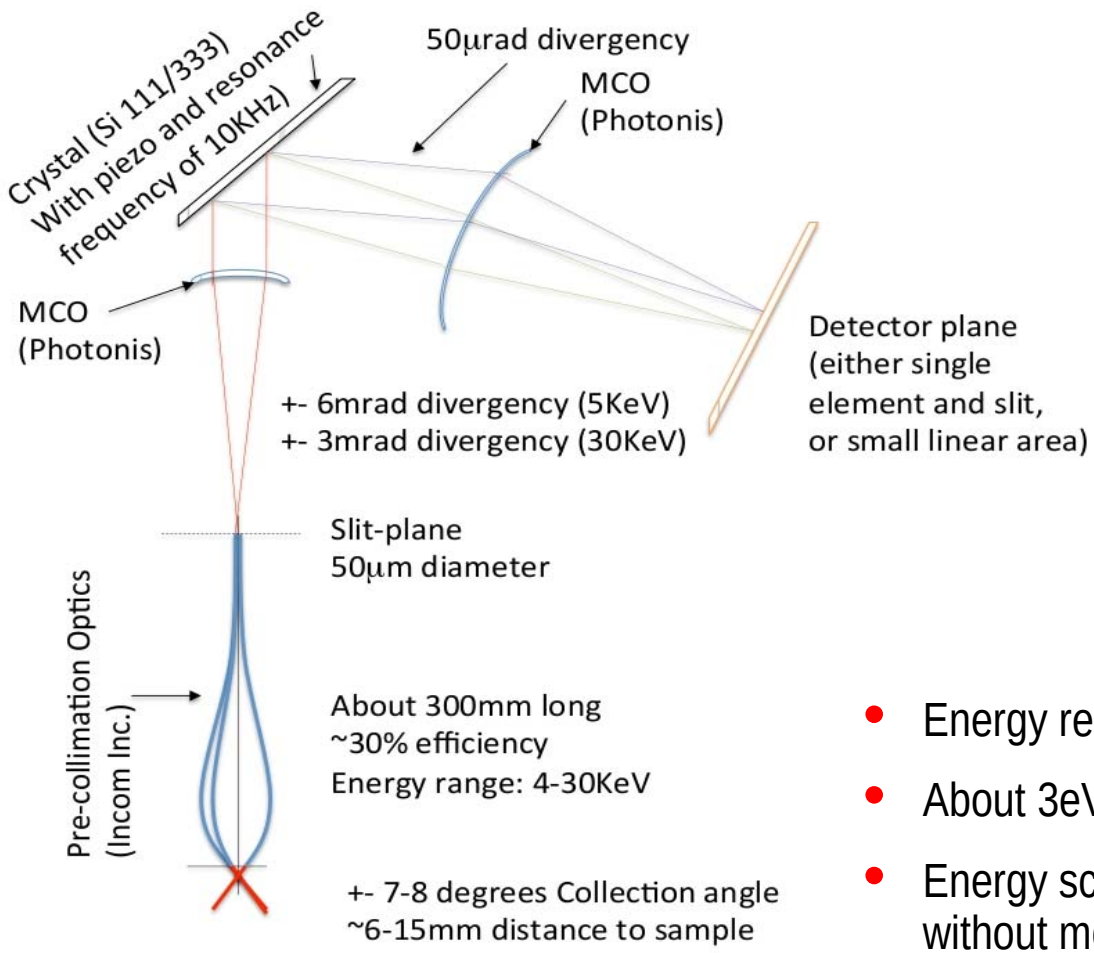




- Detector type
  - Energy resolving detector (SDD)
  - Small and fast "integrating" point detector with energetic filter:
    (using timing structure of synchrotron and analyzing pulse height to determine multiple hits)
  - Area and linear detectors to image and/or energeticly resolve
- Processing soft- and hardware (real time)
  - Fast digitization (~10GHz digitization rate)
  - Fast fitting and background determination
  - "slow" fitting and background determination (200-500MHz)
  - Software extracting spectral information from 1-D and 2-D detectors (1-10KHz)
  - Data handling (pre-selection) and saving

SPECTROMETER:
A CZERNY-TURNER SPECTROMETER

MCO: Multi Channel Optics

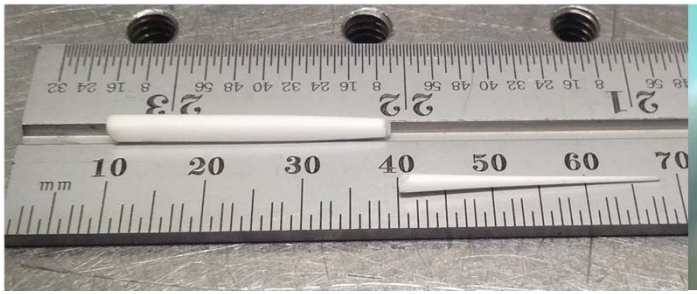


Component	Efficiency
Pre-collimation optics	25%
First MCO	65%
Crystal	95%
Second MCO	50%
Detection system	80%
Mechanics	-
Housing	-
(Detection) Total	~5-6%

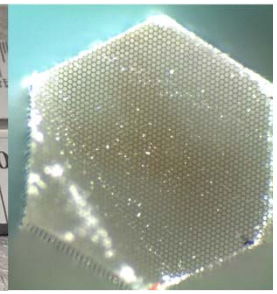
- Energy resolution of about 0.3-0.5eV @ 10keV
- About 3eV transmission @ 10KeV
- Energy scan (within ~40eV) by rocking the crystal without moving the detector arm

SPECTROMETER: LENS DEVELOPMENT

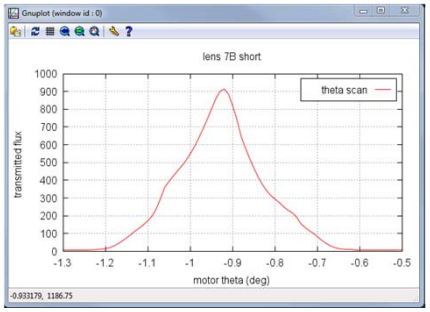
Drawing lens



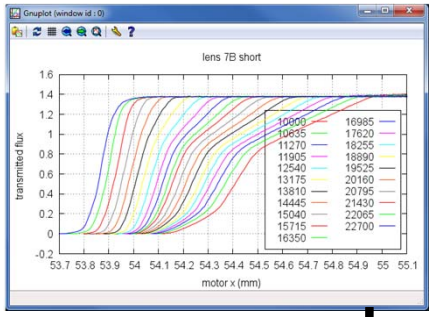
Inspecting opening

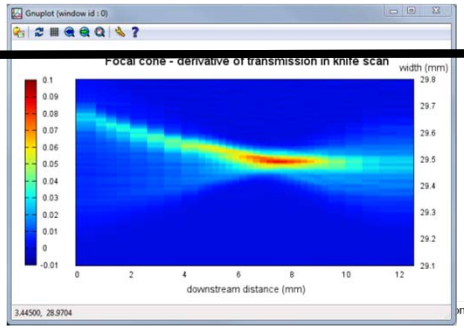


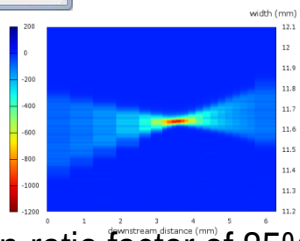
Characterizing angle dependence



Characterizing photon-field





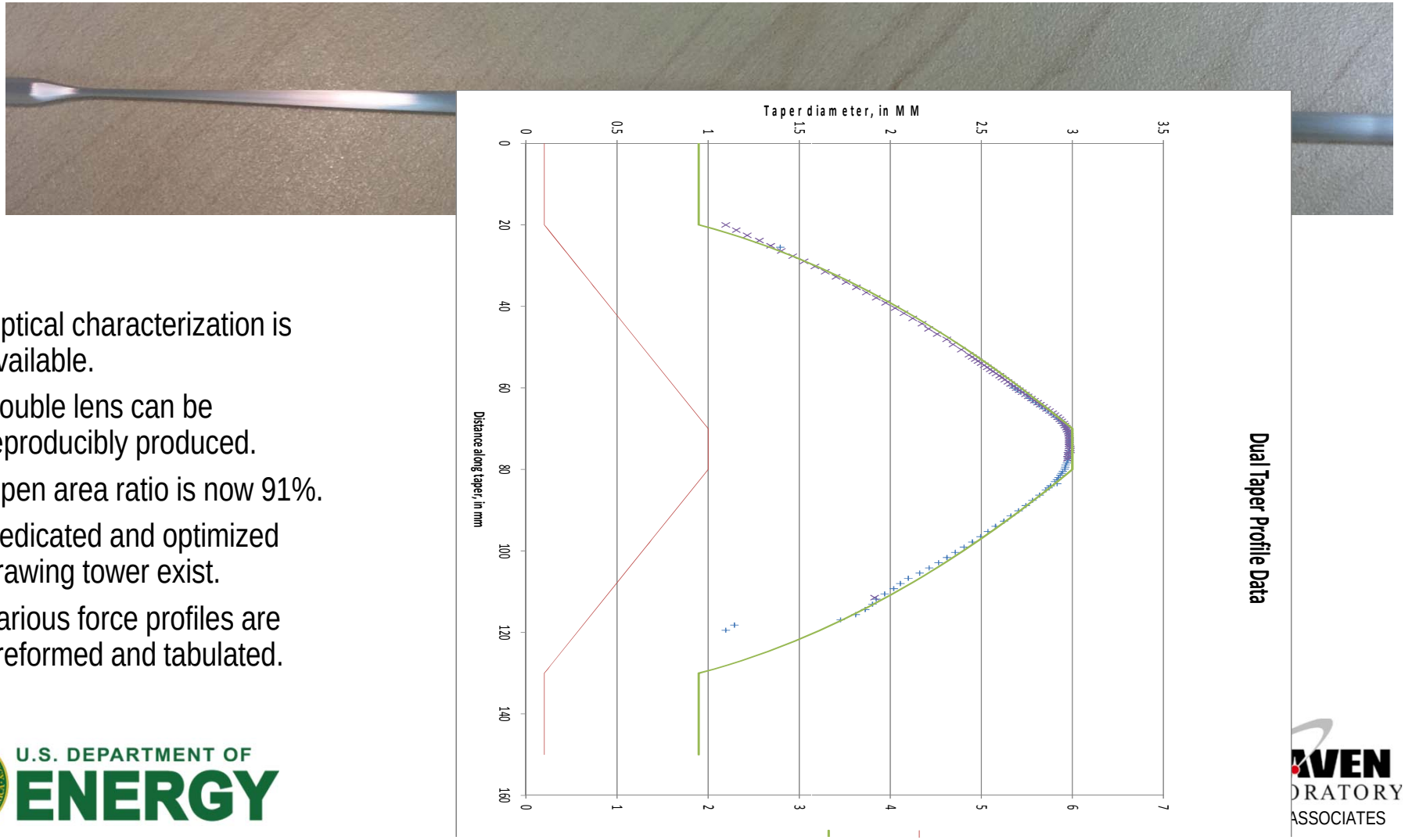


Development of collection optics has started:

- DOE STTR-proposal was approved.
- Prototyping process has started:
  - Measurement/production procedure is established
  - Second iteration has been done (in total: 12 lenses characterized full length & shortened)
  - Max efficiency: 9.4%; smallest size: 60μm
  - Next iteration step: improvement of “smooth” transition from flat to curved; changing to open-ratio factor of 85%

PROGRESS IN DRAWING PROCESS

First Full lens drawing:



- Optical characterization is available.
- Double lens can be reproducibly produced.
- Open area ratio is now 91%.
- Dedicated and optimized drawing tower exist.
- Various force profiles are preformed and tabulated.

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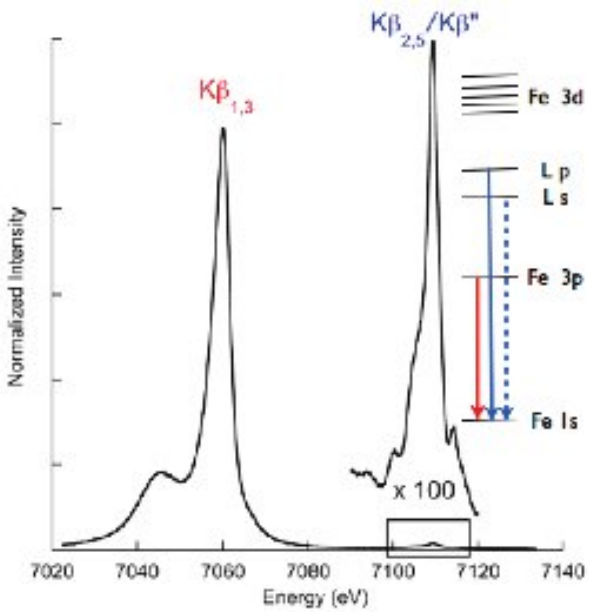
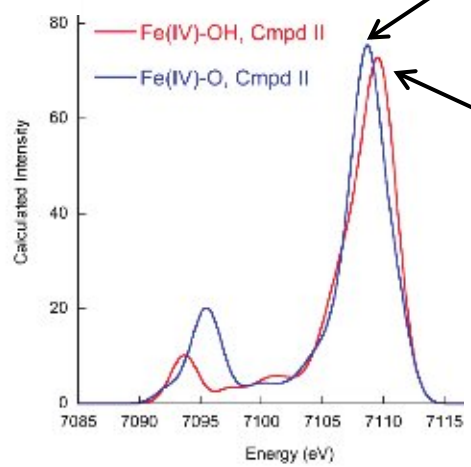
WHAT DOES ENERGY RESOLUTION BUY?



- Relaxation from valence states (instead of core levels)
- "relatively easy to calculate" by DFT
- Unprecedented visualization (for an x-ray probe) of chemical environment
- Similar information to optical RAMAN-Spectroscopy



Fe(IV)-O

Fe(IV)-OH

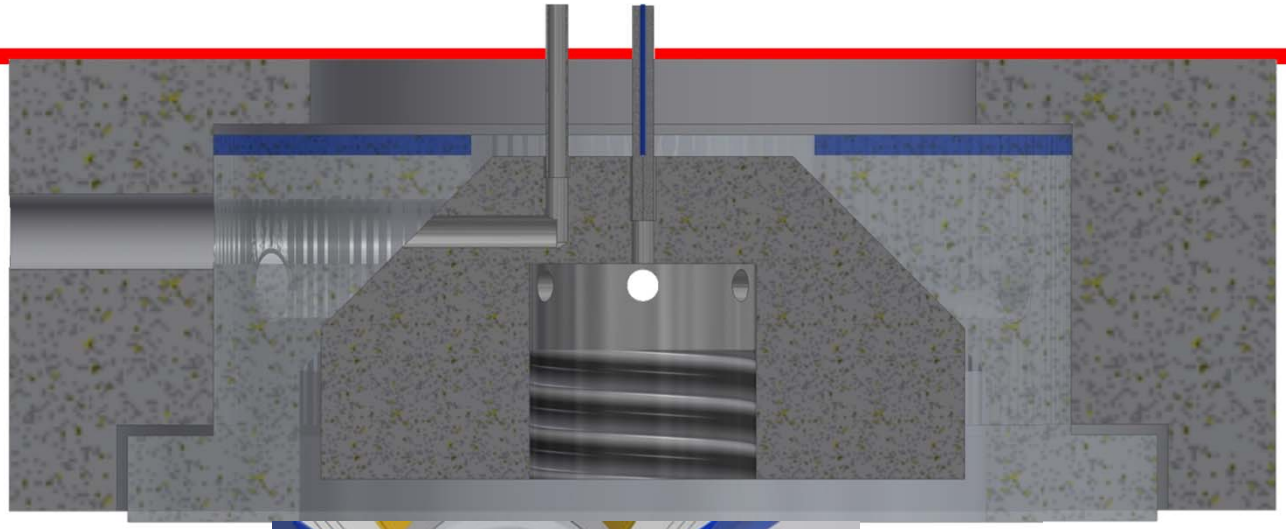
Some literature:

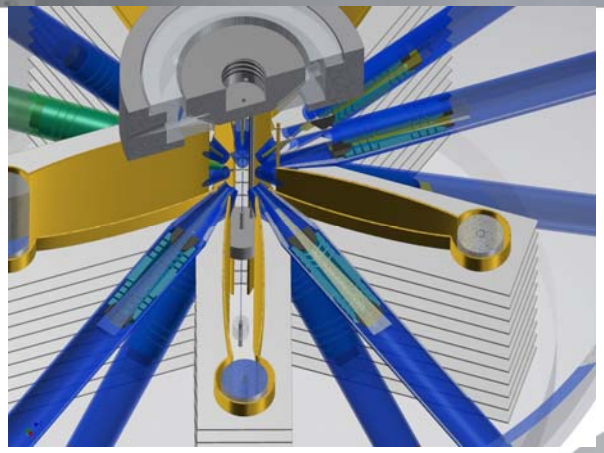
J. AM. CHEM. SOC. 2010, *132*, 9715–9727

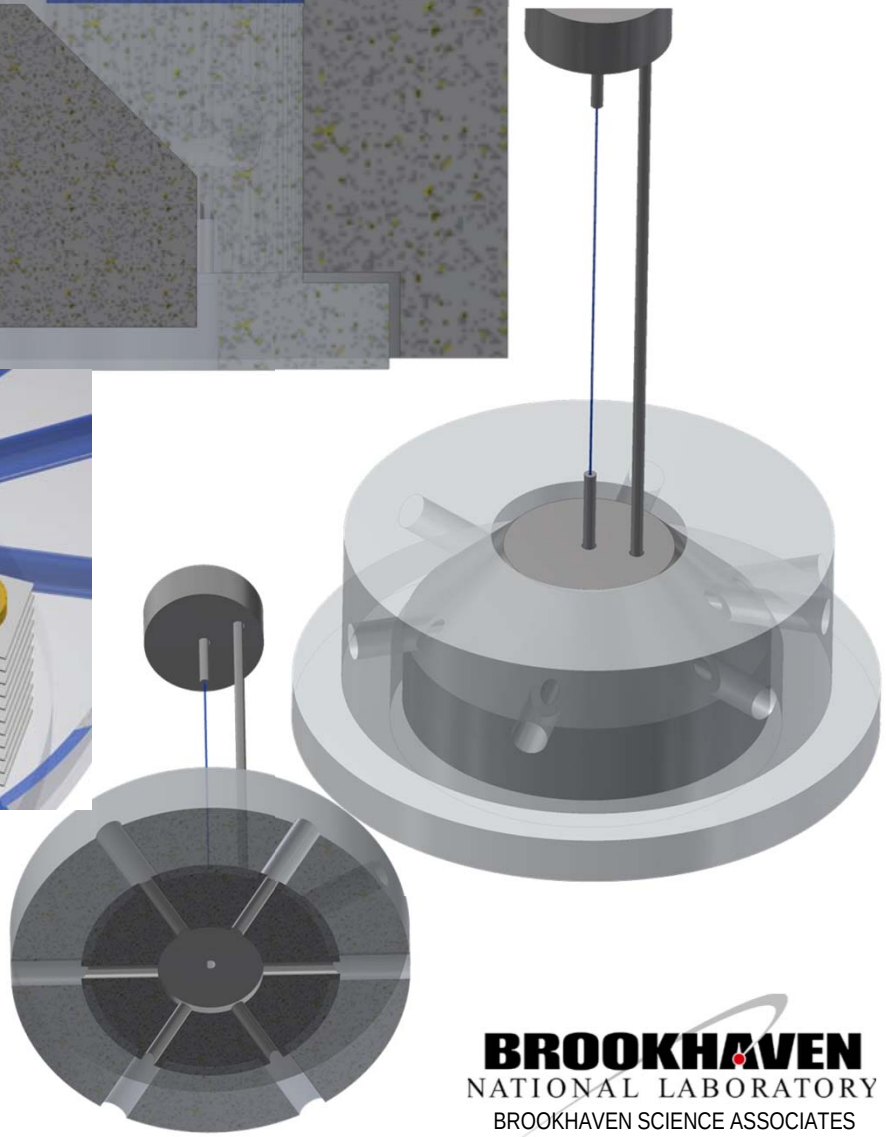
Kyle M. Lancaster *et al. Science* 334, 974 (2011)

Inorg. Chem. 2011, 50, 6767–6774

The Reactor Design







Concept:

- Reactor concept developed and reviewed
- Integration concept is developed
- Proto typing will start in the next 3 month
- Synchrotron Catalysis Consortium will be actively involved in testing

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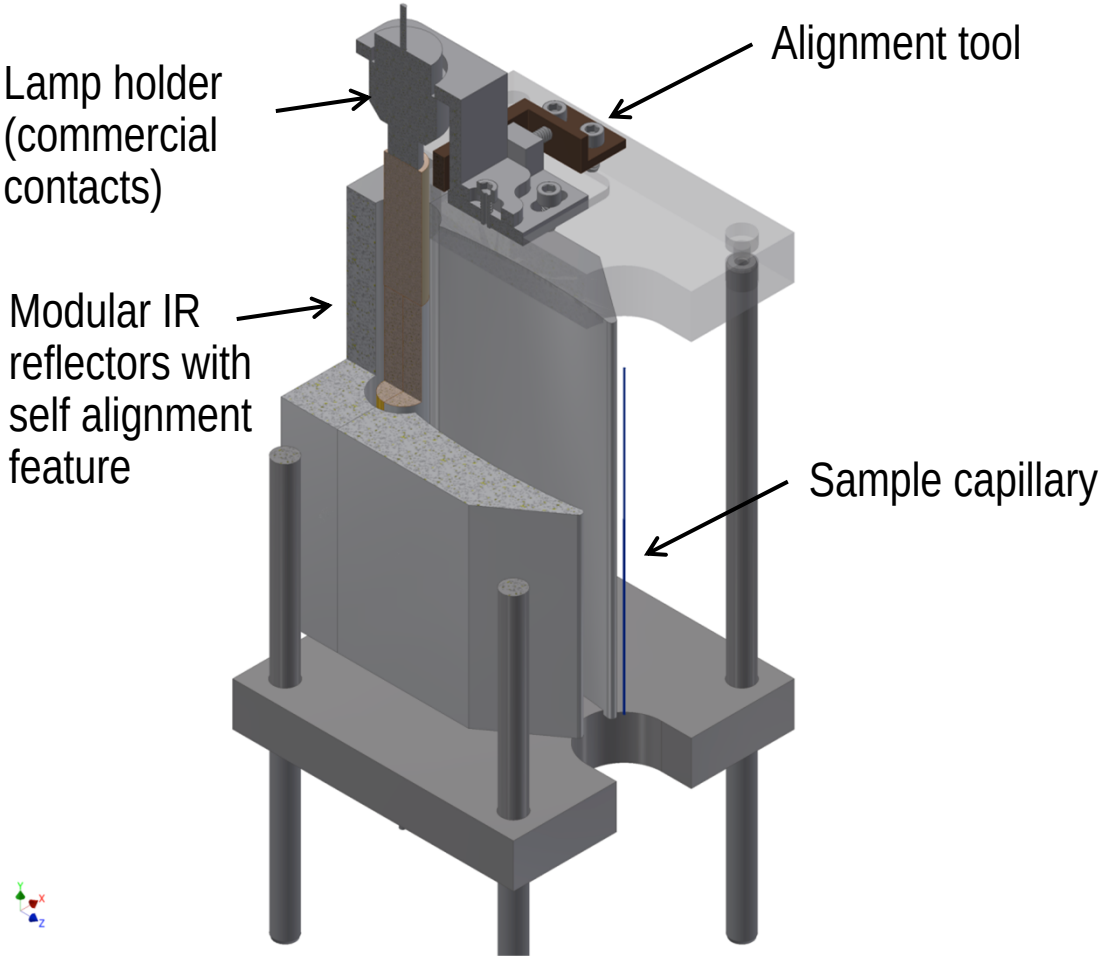
SOME MORE THOUGHTS TOWARDS HEATING



Maximal temperature: 800C

Lowest temperature: 5-10K

- IR-Heater
  - Allows to optimize wavelength for selective heating
  - Focus reduces heat load on cryo system
  - Focus allows implementations of optics
- Mechanical design is currently tested in prototypes
  - Easy access is designed in
  - Required alignment freedoms are unknown

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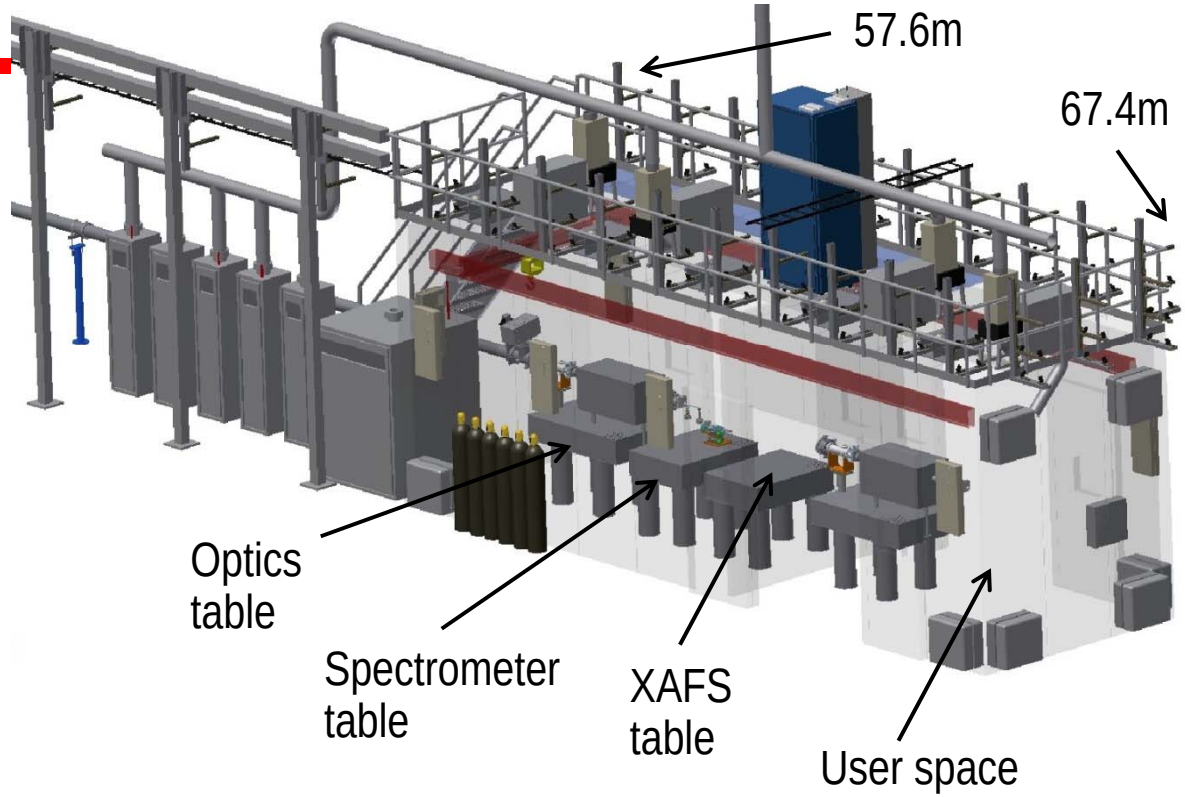
ENDSTATION & INFRASTRUCTURE

Major components:

- Detector systems:
  - XAFS detector
  - Spectrometer
- In Operando Infrastructure
  - Gas handling system
- Sample Handling System
  - Full environmental control from preparation to measurement



Five standard configuration modes:

Mode	geometry	detection
Capillary/Spectrometer	capillary	spectrometer
GI/Spectrometer	Flat surface	spectrometer
Capillary/XAFS	capillary	XAFS-detector
GI/XAFS	Flat surface	XAFS-detector
User-defined area	-	-

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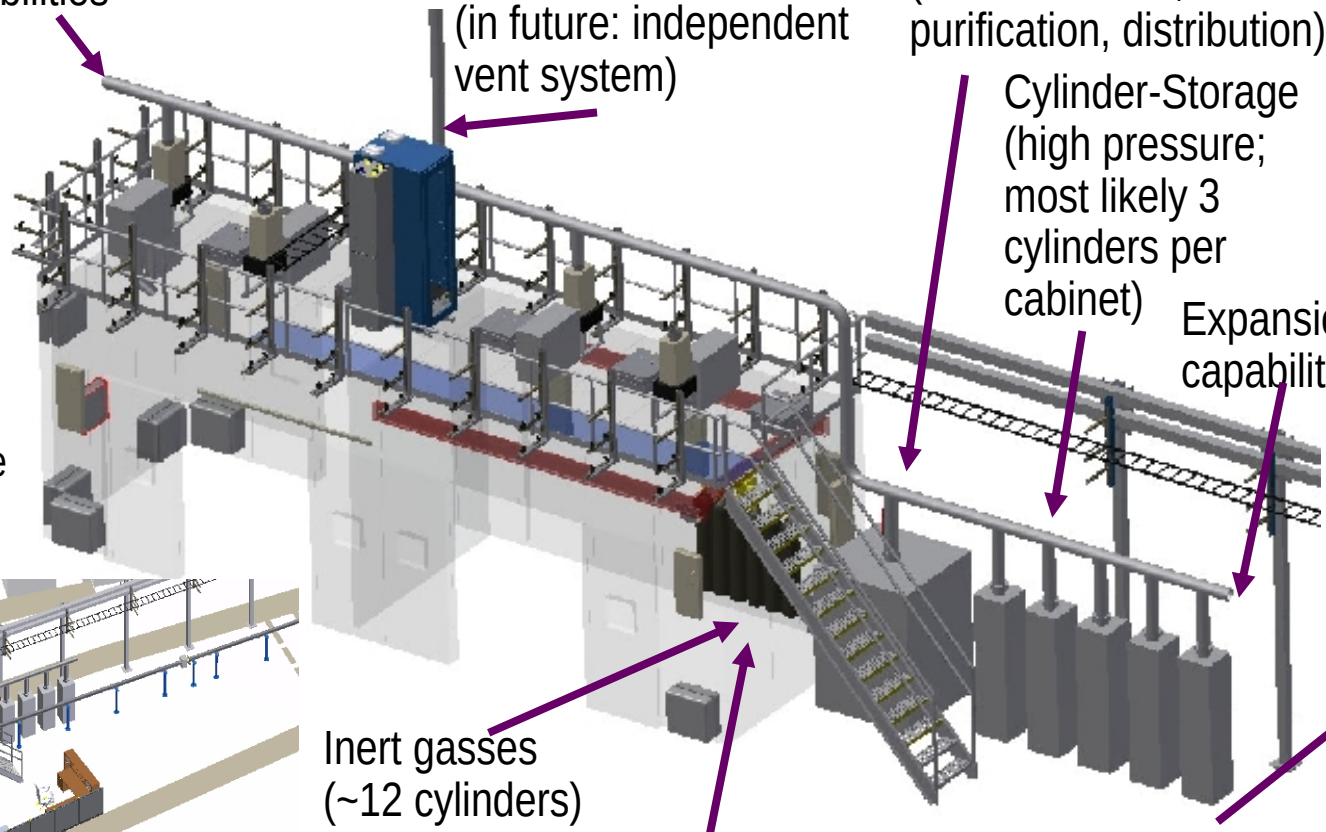
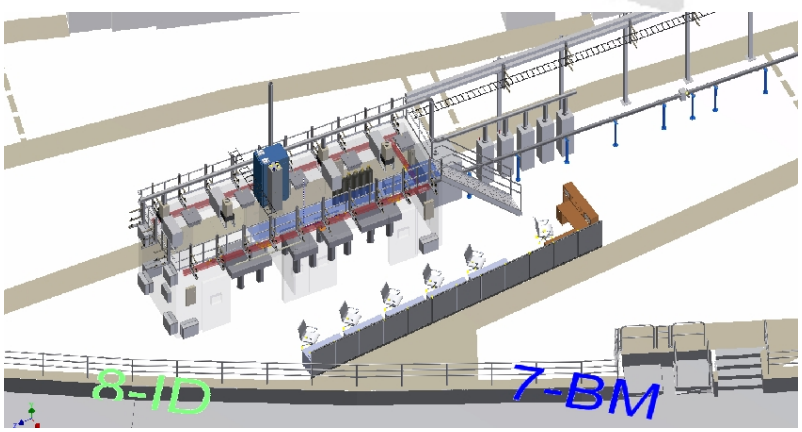
THE GAS HANDLING SYSTEM

Concept:

- 3 hazardous cabinets
  - CO, NO, NO_x
  - SH_2, + 2 optional S-gases
  - Flammable gases (3)
  - Optional: P-containing gases (3)
- Capable to feed other beamlines of the XAFS village





THE NEXT CHALLENGES FOR ISS

- Development of high speed data acquisition system (DAC) (10KHz data rate) with "asynchronous data mode" allow continuous scans
  - Scan speed profile will be programmable allowing (constant statistic throughout the scan)
  - Monochromator will scan 1 degree within 1s in both directions
- Integration of quadrupole mass specs and gas handling system into DAC
- Display software which integrates data display, simulation and data base access
- Auxiliary sample preparation area: Proposed laboratory with
  - 4 glove boxes fully equipped for catalysis, battery research, metallo organics, and general inert use (but with water)
  - Optical spectrometers (IR, Raman, UV-Vis)
  - Nano working area
  - Sample preparation area
  - Access to gas-handling system with cooling and heating

CONCLUSION

- The potential of synchrotron experiments is much higher than we see in day-to-day operations
- To benefit from high throughput beamlines we will need to address:
  - Detection efficiency and background suppression
  - Integration of focusing, detection and sample handling system
  - Integrate all hardware in data acquisition system
  - Provide appropriate programming tools which allow to focus the user to the scientific problem
- Development efforts are required to
  - Develop appropriate integrated sample environments (focus of different facilities on specific scientific areas)
  - Develop schemes to integrate detection system
  - Combine conventional detection with optics to suppress background, increase collection efficiency, and allow extreme sample conditions (moving detectors away from sample)
  - Software efforts are essential to make user friendly experiments
- We are on the way!